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TITLE. STRUCTURAL STUDIES AT ELEVATED PRESSURE AND REDUCED TEMPERATURES USING SYNCHROTRON RADIATION: APPLICATION TO $(CERIUM)_{.8}(LANTHANUM)_{.1}(THORIUM)_{.1}$

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STRUCTURAL STUDIES AT ELEVATED PRESSURES AND REDUCED TEMPERATURES USING SYNCHROTRON RADIATION: APPLICATION TO $Ce_{.8}La_{.1}Th_{.1}$

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ABSTRACT

A facility is described which has been developed at the Stanford Synchrotron Radiation Laboratory for the rapid acquisition of structural information from a sample pressurized in a diamond-anvil cell and cooled to cryogenic temperatures. The system employs a closed-cycle He-refrigerator which can be continuously operated, independent of any liquid cryogens, from a remote control station; the sample temperature can be maintained constant to better than 0.05 K. The compressive contact force between the diamond anvils, and hence the sample pressure, is also externally controlled, thereby providing remote control capabilities for both the pressure and the temperature. Preliminary data on the critical points and volume changes associated with the pressure/temperature induced isomorphic phase transition in $Ce_{.8}La_{.1}Th_{.1}$ are presented.

INTRODUCTION

The synchrotron radiation (SR) source has many advantages over a conventional, sealed-beam x-ray tube. One of the most important is the four to more than seven orders of magnitude increase in spectral brilliance available from the SR-source.[1] Largely because of this, experiments, which might require extended exposure periods with conventional x-ray sources, can often be completed in fractions of that time when SR is used. Primarily for this reason, a system to employ SR for high pressure x-ray studies has been under development for the past three years at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University.[2,3] A variety of diamond-anvil cells (DAC) have been employed; the samples are illuminated with unfiltered, heterochromatic x-ray photons, and the scattered radiation is analyzed under conditions of fixed geometry with an energy sensitive detector, so-called energy dispersive x-ray diffraction (EDXD). Recent improvements in this system have led to the routine production of high quality EDXD spectra in relatively short measurement periods, e.g., a precision of better than 0.04% in the determination of energy peak positions can be obtained with scan periods as short as 10 sec.[4] The most recent changes in this system have been to permit high pressure operations at reduced temperatures.

EXPERIMENTAL SET-UP

The experimental setup presently in use is shown in Fig. 1. The DAC was fabricated several years ago of Be-Cu, a high conductivity, high strength Cu alloy, especially developed for low temperature operations.[5] The DAC was rigidly coupled to the cold-finger of an Air Products Displex (CSW-202) He-refrigerator. This assemblage was thermally insulated with

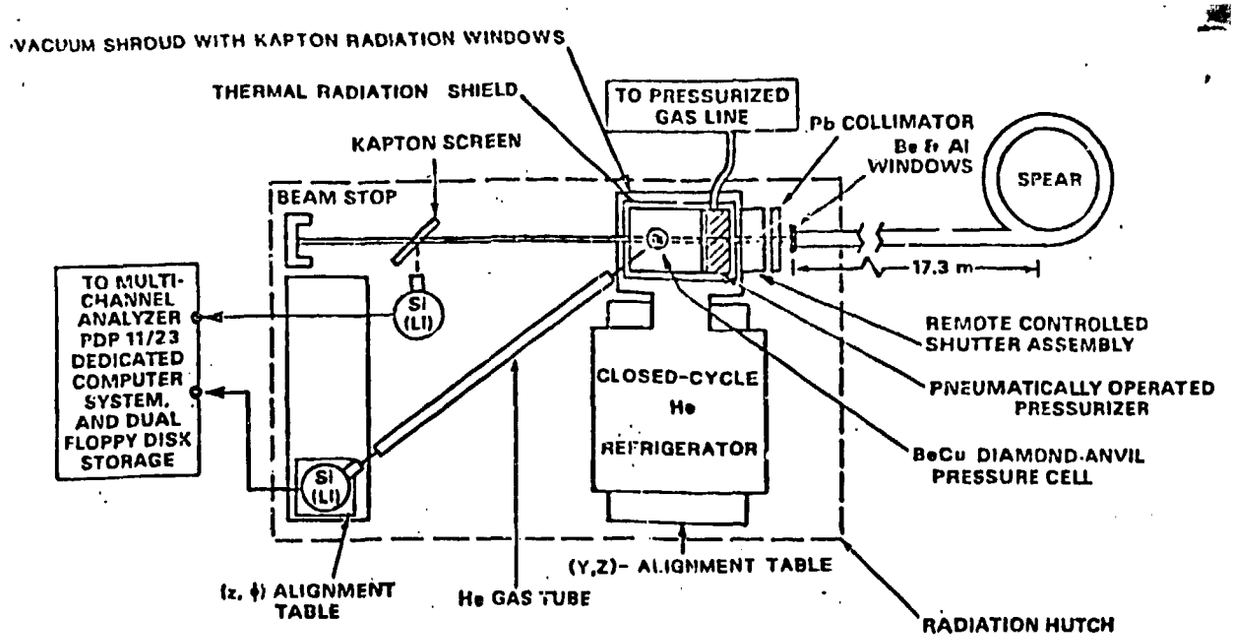

Fig. 1: Schematic drawing of the experimental setup of the closed-cycle He-refrigerator coupled to the remotely controlled Be-Cu DAC at SSRL.

several layers of aluminized mylar and contained within a stainless steel vacuum shroud provided with two large Kapton windows which served as radiation ports. The entire apparatus was rigidly mounted on a horizontal-vertical alignment table with remote adjustment capabilities, similar to those described in Ref. [3].

The temperature of the cell was controlled by the use of an Air Products temperature controller which employed either a Pt or Ge sensor, depending on the temperature range. The temperature was controlled to a value above that resulting from the cryogen by means of a manganin resistance heater wound on the cold finger, adjacent to the temperature sensors. The temperature was settable to within 0.1 K and controllable to better than 0.05 K.

The temperature of the diamond anvil was monitored with a #44-gauge Cu-resistance thermometer wound and bonded directly on the lateral faces of one of the diamond anvils; it had a room temperature (28 C) resistance of 16.63 ohms. Using a 100 ma. constant current source and a four-probe measurement technique, the change in the coil resistance was used to determine the anvil temperature, based on the calibration data of Dauphine and Preston-Thomas.[6] The diamond anvil temperature is determined to within $\pm$0.5 K at the lowest temperature, 40 K.

In order to provide pressure control at cryogenic temperatures, we employed a technique developed by one of us for variable pressure capability in a DAC coupled to a dilution refrigerator.[7] Namely, a bellows attachment was coupled to the piston in the DAC through a lever arrangement. The contact load between the diamond anvils, and hence the pressure, could be set and then increased, as necessary, by increasing the He-gas pressure in the bellows chamber. This could be accomplished from outside the hutch, and provided excellent remote control of the sample pressure and most efficient use of the SR beam time, i.e., in our initial setup the cell was clamped and isobaric data were taken as a

function of temperature. This proved to be extremely inefficient because, although spectra could be satisfactorily recorded in a few minutes, almost an hour was required before thermal equilibrium was achieved. With the bellows attachment, isothermal data are collected as a function of pressure, i.e. at each temperature setting, the pressure is swept up and down through the region of interest. As an example, during a recent run operating in this mode, 45 pressure/temperature spectra were recorded in less than three hours of operation.

APPLICATION

The first application of this system has been to study the two critical points in the pressure-temperature phase diagram of a number of Ce-rich Ce-RE-Th alloys. More specifically, the phase diagram of $Ce_{.8}La_{.1}Th_{.1}$ exhibits a first-order $\gamma - \alpha$ transition line which terminates in a critical point, completely analogous to a gas-liquid condensation. The γ and α phases are isomorphic, both being FCC structures; however, there is about a 15% decrease in the volume in going from the γ-phase to the α-phase. [8]

The addition of rare earth impurities to the Ce-Th alloys simulates "negative" pressure and leads to the disappearance of the first-order transition at ambient pressure. This "negative" internal pressure can be compensated by the application of external pressure, resulting in the "re-entrance" of a first-order transition and the appearance of two critical points at either end of the transition line; see Fig. 2.

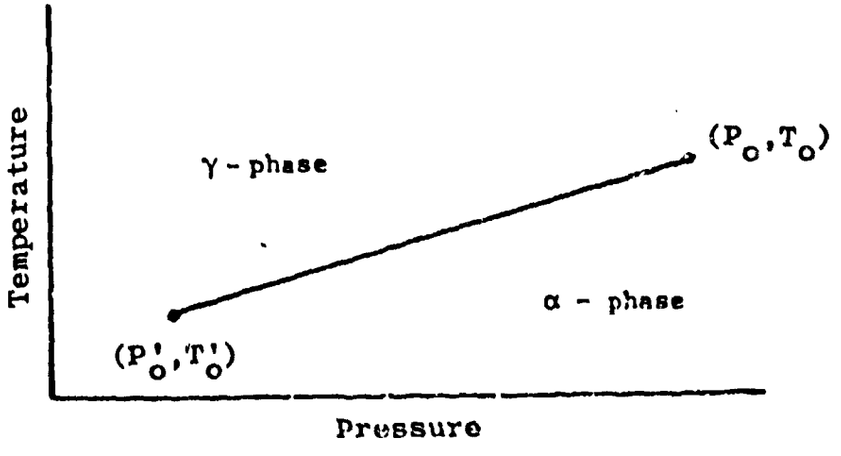

Fig. 2: Simulated phase diagram of $Ce_{.8}La_{.1}Th_{.1}$

A typical EDXD spectrum of a mixture of $Ce_{.8}Th_{.1}La_{.1}$ and NaCl taken at a pressure of about 0.5 GPa and a temperature of 60K is shown in Fig. 3. The three prominent diffraction peaks centered near 20 keV photon energies were used for the actual measurements; the NaCl-(200) peak served as an internal pressure calibrant. Several fluorescence peaks arising from the sample are also seen in the spectrum.

The effect of the γ-α phase transition is demonstrated in Fig. 4. The four scans, T-1 through T-4, were made at progressively lower temperatures and approximately constant pressures. The temperature decrement between each scan was approximately the same; this is evidenced by the relatively constant shift to higher energies of the NaCl-(200) peak. The two peaks coming from the sample however, the Ce-La-Th-(111) and -(200) peaks, both show small shifts in going from T-1 to T-2 and from T-3 to

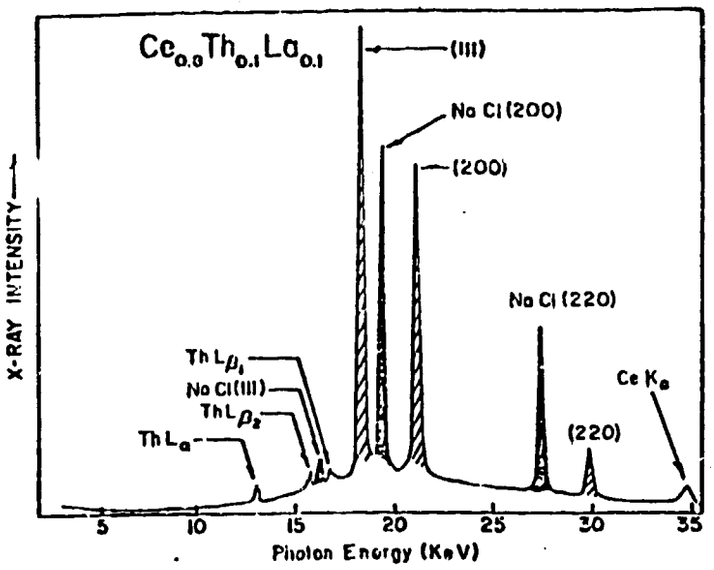

Fig 3: EDXD spectrum for $Ce_{.8}La_{.1}Th_{.1}$ at 0.5 GPa and 60 K.

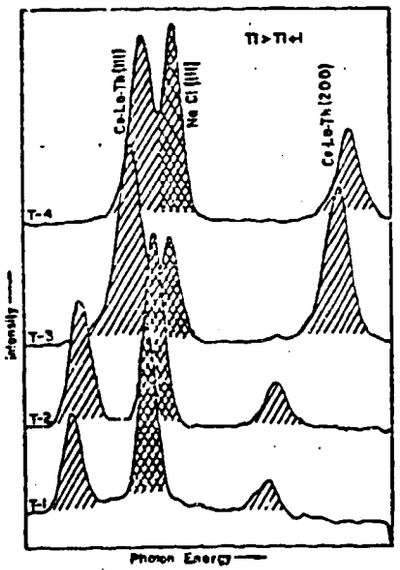

Fig. 4: Temperature shift of EDXD spectr

T-4, but in each case, the shift in going from T-2 to T-3 is much greater. This is the result of the 15% volume change associated with the phase transition.

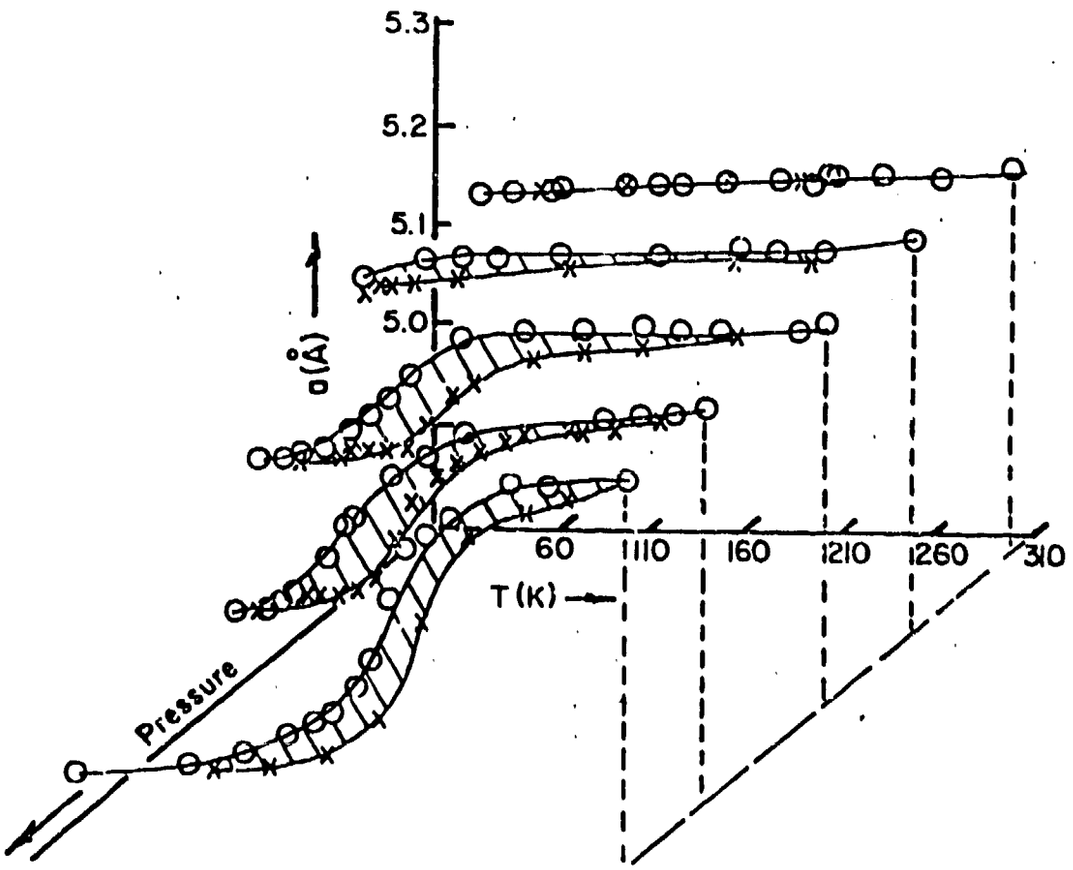

Fig. 5: Effect of pressure on the temperature dependence of the unit cell parameter in $Ce_{.8}La_{.1}Th_{.1}$.

The hysteretic nature of the transition and the effect of moving through the lower critical point (P_o',T_o') are represented in Fig. 5 where the temperature dependence of the unit cell parameters of the Ce-La-Th are plotted at approximately constant pressure increments. The circles represent data taken while cooling, the crosses represent data taken while warming; in both cases, under conditions of thermal equilibrium.

Additional research on the transition in $Ce_{.8}Th_{.1}La_{.1}$ is presently underway. Work is planned for the immediate future to also study the critical exponents near the critical points for five other "re-entrant" alloys, viz., $Ce_{.9-x}La_xTh_{.1}$ (x=0.15), $Ce_{.9-x}Gd_xTh_{.1}$ (x=0.15 & 0.20), and $Ce_{.9-x}Eu_xTh_{.1}$ (x=0.03 & 0.04). Moreover, we are presently engaged in theoretical calculations to extend the equation of state calculations for NaCl to low temperatures and thereby to provide a convenient low temperature pressure gauge.

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